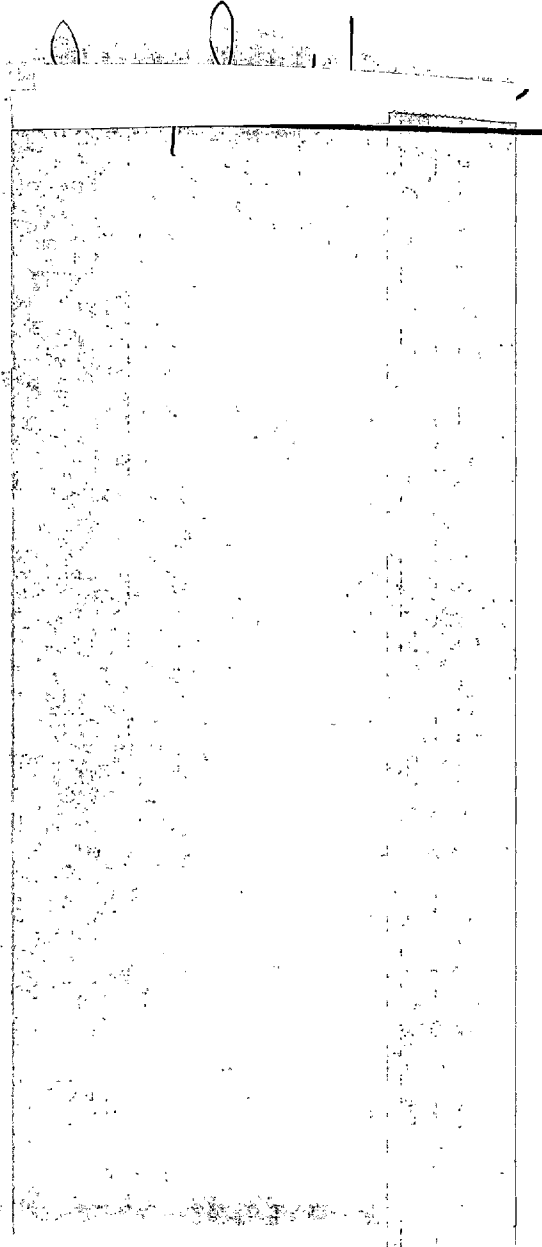


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PART ONE

DETERMINATION OF THE ACIDITY OF VERY WEAK ACIDS

PART TWO

THE REACTION OF ETHYL ORTHOTHIOFORMATE AND
RELATED COMPOUNDS WITH POTASSIUM AMIDE IN
LIQUID AMMONIA

A THESIS

Presented to
the Faculty of the Graduate Division

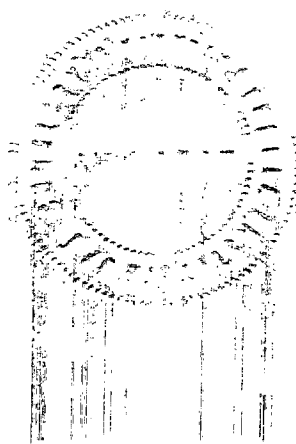
By

Gary G. Hammer

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

Georgia Institute of Technology

April 1962



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PART ONE

DETERMINATION OF THE ACIDITY OF VERY WEAK ACIDS

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LIQUID AMMONIA

Approved:

[Signature]

Date approved by Chairman:

May 4, 1962

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SUMMARY

Part One

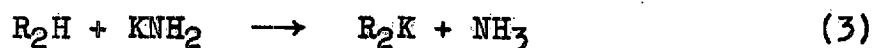
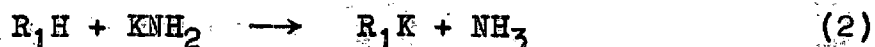
There have been several previous studies on the acidity of very weak acids, i.e. acids whose acidity is too weak to measure in water. Only two of these studies, however, have been devoted to measuring quantitatively the pK_a 's of very weak acids. These workers measured equilibrium constants for reactions of the type



The position of the equilibrium is determined by the difference in acidity between the two compounds, R_1H and R_2H . The pK_a 's of a group of compounds were determined by a set of interlocking experiments (i.e. one acid was common to at least two different equilibria) in which the pK_a of one of the compounds had already been reported. However, because of inaccurate physical methods, poor ion-solvating solvents, and large acidity differences between compounds, only minimum pK_a values were actually measured. It was the intent of our work to find a more reliable method for determining pK_a 's. It seemed to us that a better ion-solvating solvent could be found, as well as a better method for measuring the equilibrium constants.

Of the solvents studied ethylenediamine was found to be unsatisfactory because an ethylenediamine solution of its potas-

sium salt could not be prepared in a pure state, and t-butylamine was unsuitable because its potassium salt was insoluble in the parent amine. Liquid ammonia was found to be suitable, and a method utilizing potassium amide as the base was developed. The acids used were all strong enough to react quantitatively with potassium amide, thus

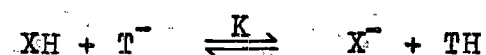


Our technique utilized this property. In a special spectrophotometric cell was placed a mixture containing known amounts of two acids of comparable acidity, and a measured amount of a standard potassium amide solution in liquid ammonia was added. The total acid concentration was greater than the base concentration, thus the base was completely consumed. In such a case Equations (2) and (3) combine to give



As mentioned before the position of the equilibrium depends upon the acidity difference between the compounds, R_1H and R_2H . Our technique was to use one acid whose conjugate base was colorless, and another acid whose conjugate base was colored and had a known extinction coefficient. Since the amount of added amide was known, and the amounts of the two acids originally present were also known, it was only necessary to measure the concentration of the colored species at equilibrium in

order to calculate the equilibrium constant for a particular reaction. This measurement was made spectrophotometrically. The equilibrium constant (K) was measured for the reaction of 9-phenylxanthene with potassium p-toluidide,



where XH and X^- are 9-phenylxanthene and 9-phenylxanthide ion, respectively, and TH and T^- are p-toluidine and p-toluidide, respectively, and the value of K was found to be 4.5. Since the equilibrium constant for a reaction of this type is a quantitative measure of the difference in acidity between the two acids, 9-phenylxanthene is 0.65 pK_a units stronger than p-toluidine, i.e. ΔpK_a ($-\log K$) is 0.65. With this procedure it is now possible to determine the pK_a 's of more compounds and to determine them over a wider range of acidities.

During the course of this study a few experiments were run to determine whether or not potassium t-butoxide in dimethyl sulfoxide was a strong enough base to convert any of the very weak acids to their conjugate bases. Our experiments showed that t-butoxide ion in dimethyl sulfoxide was at least as strong a base as the amide ion in liquid ammonia. This indicates that this solvent-base pair could be of use in determining the acidity of very weak acids.

Part Two

During the course of the study on the acidity of very weak acids, we investigated the reaction of tris(ethylthio)meth-

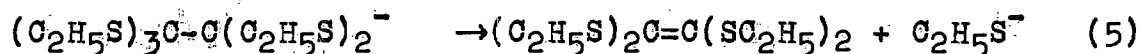
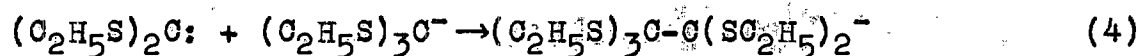
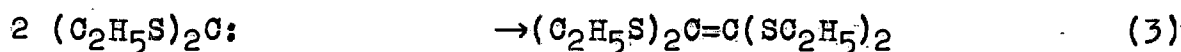
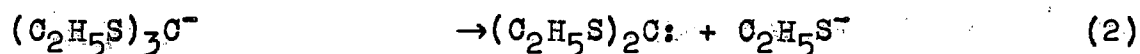
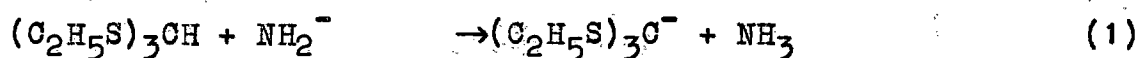
ane and some related compounds with potassium amide in liquid ammonia. These compounds were being considered for use in the acidity study. Before they could be used, however, the possibility of side reactions under the conditions of the acidity experiments had to be investigated.

Bis(methylthio)methane was found to react with potassium amide in liquid ammonia in the manner previously reported. No evidence for competing side reactions was found.

Bis(phenylthio)methane was also investigated. The results obtained were rather inconclusive. Some evidence for side reactions was found; however, the reaction needs further investigation.

Tris(ethylthio)methane was found to undergo α -elimination when reacted with potassium amide in liquid ammonia.

The products obtained from the reaction suggest the following reaction scheme:



This is the first reaction in which evidence has been obtained for a methylene intermediate with two sulfur atoms attached to

the methylenic carbon. The methylene intermediate is presumably stabilized by p and d orbital resonance. The investigation of this reaction is by no means complete. Additional work should be done to learn what other reaction paths are available to the bis(ethylthio)methylene under the reaction conditions.

PART ONE

DETERMINATION OF THE ACIDITY OF VERY WEAK ACIDS

CHAPTER I

INTRODUCTION

The purpose of this research was to measure pK_a values of very weak acids. Very weak acids¹ are defined as those acids whose acid strength is too small to measure in water. In this study the weak acids used were aromatic amines and arylated hydrocarbons.

The first quantitative measurements of pK_a values for such compounds were those of Conant and Wheland.² These workers studied equilibria of the type



The conjugate bases of most of the hydrocarbons used in these studies are highly colored. Whenever possible, this property was used as a means of measurement. Conant and Wheland² measured the concentrations of the anions by two methods, (a) colorimetry and (b) carbonation and analysis of the acid mixture.

McEwen³ extended this work to include a larger number of acids, and also improved upon the method of measurement by

¹J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 49-50.

²J. B. Conant and G. W. Wheland, J. Am. Chem. Soc., 54, 1212 (1932).

³W. K. McEwen, ibid., 58, 1124 (1936).

using colorimetry, spectroscopy, and polarimetry. After measuring the equilibrium constant for a reaction such as that shown in Equation 1, either R_1H or R_2H was used in another experiment with a different acid, R_3H . As was the case with R_1H and R_2H , R_3H was chosen such that its acidity was relatively near that of the compound with which it was to be compared. A series of such overlapping experiments, including one with an acid whose pK_a had been reported, were run. If

Table 1. Acidity Scale of Very Weak Acids³

<u>Compound</u>	<u>pK_a</u>
Methyl alcohol (standard)	16
Ethyl alcohol	18
t-Butyl alcohol	19
9-Phenylfluorene	21
Diphenylamine	23
Fluorene	25
p-Toluidine	27
9-Phenylxanthene	29
4-Biphenylyldiphenylmethane	31
Triphenylmethane	33
Diphenyl-1-naphthylmethane	34
Diphenylmethane	35
1,1-Diphenylpropene	36
Cumene	37

the two compounds compared differed in pK_a by 2 units, the reaction shown in Equation 1 would proceed to 90 per cent completion when equivalent amounts of the two compounds were used. When a five-fold excess of one of the compounds was used, a difference of 0.4 pK_a units corresponded to 90 per cent completion. The values in the range 33-37 were obtained from experiments of the last type, although they were shown as

having ΔpK_a 's of 1. All of the reactions studied went to at least 90 per cent completion, so the pK_a differences shown in Table 1 are minimum values of either 0.4 or 2 units. Thus not one quantitative comparison of acidities was made and all of the reported pK_a 's, like the ΔpK_a 's are merely minimum values. The unreliability of the pK_a 's stems partly from large differences in acidity between compounds and the insensitivity of the methods of measurement.

In other work in this area an attempt has been made to relate rates of deuterium exchange^{4,5} to acidities. Such a relationship may be valid for a series of closely related compounds, but it is known not to hold in general. For example, nitroethane, whose pK_a is 8.6, undergoes first order ionization in water with a rate constant of $2 \times 10^{-6} \text{ min}^{-1}$, whereas for bis(carbethoxy)methane (pK_a 13.3) k_1 is $2 \times 10^{-3} \text{ min}^{-1}$.⁶ These data show the inaccuracy of measuring acidity in terms of rate of proton removal or rate of deuterium exchange.

The general unreliability both of reported pK_a 's and the methods used for determining them suggested a further investigation of the problem, and in particular, the development of a reliable method suitable for measuring the position

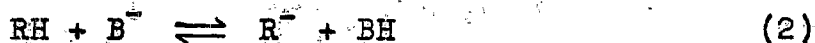
⁴A. I. Shatenshtein, Doklady Acad. Nauk S. S. S. R., 60, 1029 (1950); C. A., 44, 5194 (1950).

⁵H. Hart and R. E. Crocker, J. Am. Chem. Soc., 82, 418 (1960).

⁶R. G. Pearson and R. L. Dillon, ibid., 75, 2439 (1953).

of equilibria of the type shown in Equation 1. To do this two things had to be done. The first was to find a better solvent for the reactions. Conant and Wheland² used ether as the solvent for their reactions. McEwen³ used ether for some reactions, and benzene for others. Neither ether nor benzene is a good ion-solvating medium, and Conant and Wheland² and McEwen³ had to assume an equal amount of dissociation for their salts. Thus it was felt a better ion-solvating solvent could be found. The second thing to be done was to find a better method for measuring the concentrations of the anions. Another improvement would be to use the conjugate base of the solvent, if possible, as the base in these reactions. This would simplify the procedure by making the solvent one of the products of the reaction. In addition, the problem of handling the alkali-metal salts would be disposed of.

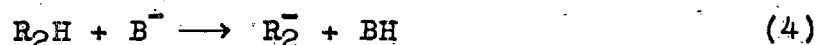
For those acids of strength comparable to that of the solvent, the technique would be to add a measured quantity of the base to a measured quantity of an acid



Since BH is the solvent, it is necessary only to measure the concentration of R^- in order to calculate the concentrations of each of the species present at equilibrium.

When an acid is much stronger than the solvent, the technique must be changed, since in this case, the acid will consume the base, i.e. the conjugate base of the solvent, until

the less abundant of the two has been almost completely consumed. Thus if there is an excess of base present, the acid will be completely converted to its conjugate base. For this reason it is necessary to use a technique somewhat similar to that of Conant and Wheland² and McEwen.³ A mixture of two acids of comparable strength is used. The mixture containing measured amounts of two acids is treated with a measured amount of base



If the total acid concentration exceeds the base concentration, the base will be completely consumed, and the total concentration of the two anions, R_1^- and R_2^- , will be equal to that of the added B^- . The relative acidities of R_1H and R_2H may be expressed in terms of the following combination of Equations (3) and (4)



The concentration of each species present at equilibrium can be calculated if the concentrations of the individual anions are known. As was mentioned previously, the conjugate bases of many of the hydrocarbon acids are highly colored, and if Beer's law is obeyed a spectrophotometric method should be suitable for measuring their concentrations. Conant and Wheland² and McEwen³ used a colorimetric method, which leads us to suppose that Beer's law is obeyed by these compounds.

CHAPTER II

PROCEDURE

Selection of Solvent-Base System

Ethylenediamine-N-Potassioethylenediamine.--The first solvent-base system investigated was ethylenediamine-N-potassioethylenediamine. A solvent was desired that could be handled at room temperature, i.e. without cooling, as well as itself being a very weak acid. If the solvent is a very weak acid, its conjugate base would be a strong base. It was thought that ethylenediamine, b.p. 114° , would fit these requirements. Since ethylenediamine is an organic compound, it should be a good solvent for the weak acids and should be better than ether at solvating ions since it has a higher dielectric constant, 16,⁷ as compared with a value of 4⁸ for ether.

N-Potassioethylenediamine was chosen as the base over the other alkali-metal salts of ethylenediamine, because we felt that the potassium salt would have the highest solubility, and because it and the potassium salts of the weak acids studied should be the most highly dissociated of the salts of the three alkali-metals -- lithium, sodium, and potassium -- that

⁷A. H. White and S. O. Morgan, J. Chem. Phys., 5, 655 (1937).

⁸R. J. W. LeFevre, Trans. Faraday Soc., 34, 1127 (1938).

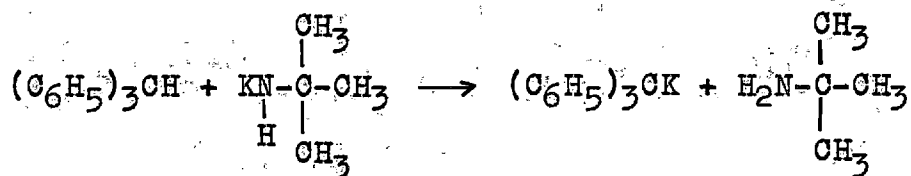
are readily available. This is known to be the case for the salts of ammonia.⁹ Since our analytical method was to be a spectrophotometric one, it was necessary that the solutions of N-potassioethylenediamine be colorless or at worst pale yellow. All attempts to prepare such colorless solutions yielded only highly colored ones. In a typical experiment a piece of potassium metal (approx. 3 mm. on an edge) was placed in 100 ml. of purified ethylenediamine, and the solution was refluxed until the original blue color, characteristic of solutions of alkali metals in amines, had faded. The color of the solution at this time was usually red or orange. Occasionally it was green. All experiments were carried out under an atmosphere of dry nitrogen. Experiments with sodium metal, using the same conditions, gave results similar to those obtained with potassium. When lithium metal was used instead of potassium or sodium, N-lithioethylenediamine¹⁰ was obtained. The solution was colorless, however, a large amount of a tan precipitate was present in the bottom of the flask, N-lithioethylenediamine. Because of the fact that colorless solutions of the sodium and potassium salts were not obtained, while the lithium salt would probably react with weak acids to give lithium compounds with considerable covalent character, the ethylenediamine-alkali metal salt system was dropped.

⁹W. W. Hawes, J. Am. Chem. Soc., 55, 4422 (1933).

¹⁰L. Reggel, S. Friedman, and I. Wender, J. Org. Chem., 23, 1136 (1958).

t-Butylamine-Potassium t-Butylamide.--Organic amines and their conjugate bases seemed to us to be the best possibilities for a suitable solvent-base system. Thus we next considered t-butylamine-potassium t-butylamide. Although t-butylamine boils near room temperature, b.p. 45° , it has the advantage of not having hydrogen atoms alpha to the amine group which decreases the chances for oxidative side reactions. The dielectric constant of t-butylamine does not appear to have been reported.

The potassium salt was prepared by refluxing t-butylamine with a liquid Na-K alloy (1 part sodium to 5 parts potassium by weight). This was done because the melting point of potassium is above the boiling point of t-butylamine. Potassium t-butylamide appeared to have been formed, as evidenced by the tan precipitate that formed. This solid reacted with triphenylmethane to give the bright red color of the triphenylmethide ion



There was no evidence of reaction in the solution above the solid, only at the surface of the solid. Since the solubility of the amide was so low, further work with this amine-amide pair was dropped.

Liquid Ammonia-Potassium Amide.--The work of Katayama¹¹ demonstrated the suitability of liquid ammonia-potassium amide for this type of study. Liquid ammonia has a dielectric constant of 22 at -34° .¹² Because potassium amide and the conjugate bases of the weak acids react readily with oxygen and water, it was necessary that we make our studies in an atmosphere as free from these substances as possible. The high-vacuum system shown in Fig. 1 was assembled to enable us to do this. With this system we were able to work in an ammonia atmosphere free from oxygen and water.

After assembling the system, it was closed at points A, C, E, F and G and pumped on for several days to allow the components to out-gas. All stopcocks were open during the out-gassing period. In order to test for completeness of out-gassing and for leaks, the rate of increase in pressure (with the system closed to the pumps) was measured for the whole system and for the Stokes gauge alone. Out-gassing was considered complete when the rate of pressure-increase was less than 1.0 μ /min. The system was considered to be as free of leaks as possible when its rate of pressure-increase compared favorably with that of the Stokes gauge alone. The Stokes gauge was considered to be the most likely source of incurable leaks, because it contained several tygon tubing connections. The slowest

¹¹M. Katayama, unpublished work from this laboratory.

¹²H. M. Grubb, J. F. Chittum, and H. Hunt, J. Am. Chem. Soc., **58**, 776 (1936).

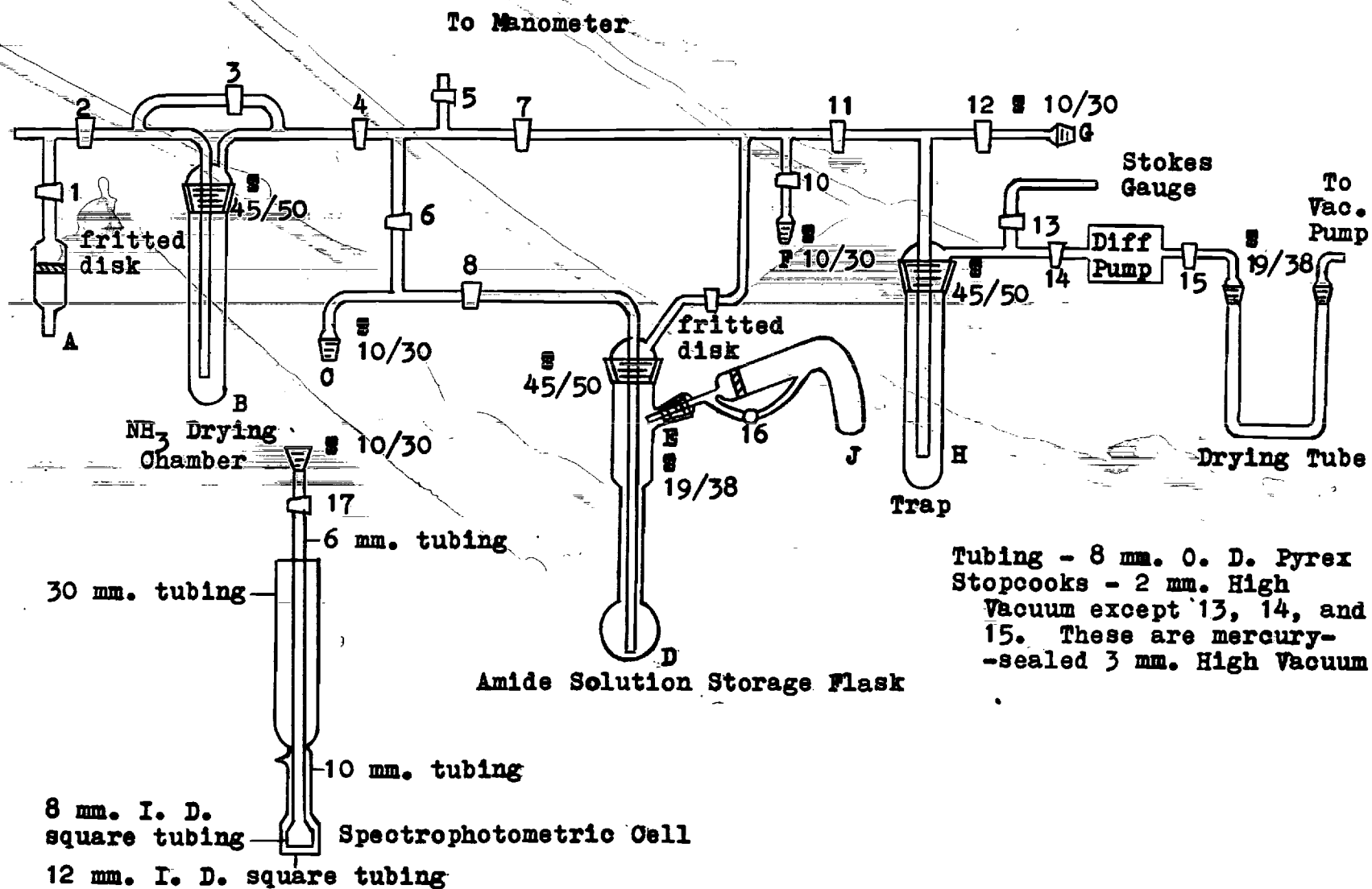


Figure 1. High Vacuum Apparatus

leak rate obtained was $0.45 \mu/\text{min.}$ for the complete system and $0.60 \mu/\text{min.}$ for the Stokes gauge. The highest vacuum initially available was 0.5μ . After the system had been in use for awhile, the highest vacuum that could be obtained was of the order $4-6 \mu$. The loss in vacuum was not due to leaks but to the desorption of sorbed materials in the absorbant in the Stokes gauge. The pumps used were a Cenco High-Vac vacuum pump in conjunction with a mercury diffusion pump. All joints and stopcocks were lubricated with Apiezon type-N grease.

The major steps yet to be accomplished were: (1) the introduction and drying of the liquid ammonia, (2) the preparation of a standard potassium amide solution and (3) the transfer of the potassium amide solution. The first of these was accomplished in the following manner. The drying chamber (B) was removed, two or three medium sized pieces of sodium metal were placed in it, and it was replaced in the system. The sodium was used as a drying agent for the liquid ammonia. Next the system was flushed thoroughly with gaseous ammonia to remove as much oxygen and water vapor as possible. Stopcock No. 11 was closed during the flushing operation. Next point F was capped, and stopcocks No. 3, 7, and 8 were closed. At this time ammonia gas was entering the system at A and leaving at C, and all stopcocks were open except Nos. 3, 7, 8 and 11. The drying chamber (B) was immersed in a Dry Ice-acetone bath, and approximately 120 ml. of ammonia was condensed in it. Points A and C were capped, stopcock No. 4 was closed, stopcock

No. 11 was opened, and the system was pumped down. The vacuum and diffusion pumps were running at all times. Stopcock No. 3 was opened. Now by closing No. 11 and opening No. 4 and then closing No. 4 and opening No. 11, the remaining uncondensable gases to the left of No. 4 were removed. At this point stopcocks No. 1, 2 and 3 were closed permanently. All stopcocks were now open except Nos. 1, 2, 3 and 4. The next steps were taken to remove the last vestiges of oxygen in the vacuum line. Stopcock No. 11 was closed, No. 4 was opened, and the cooling bath was removed from B. Ammonia was allowed to evaporate into the system to a pressure of 10-20 mm. less than atmospheric pressure. At which time stopcock No. 4 was closed, B was immersed in the cooling bath, stopcock No. 13 was closed, No. 11 was opened, and the system was again evacuated. Stopcock No. 13 was not reopened until most of the ammonia was removed, i.e. not until the pressure as measured by the manometer ceased to change. This evaporation and evacuation operation was repeated at least twice. At this juncture stopcocks No. 10, 11 and 12 were closed. This left all stopcocks open except Nos. 1, 2, 3, 4, 10, 11 and 12.

The next step was to prepare the standard solution of potassium amide in liquid ammonia. In the potassium amide reaction chamber (J) had been sealed a weighed amount of potassium metal in a sealed ampoule, a bar magnet encased in glass, and platinum black catalyst. When the oxygen had been removed, an external magnet was used to break the potassium ampoule by

using it to raise and drop the magnet inside the chamber. Next, sufficient ammonia to cover the catalyst was distilled into the reaction chamber. This was done in the following manner. The end of the reaction chamber (J) was immersed in a Dry Ice-acetone bath, stopcock No. 4 was opened, and the cooling bath was removed from B. When sufficient ammonia had been distilled into J, B was again immersed in a Dry Ice-acetone bath, and stopcock No. 4 was closed. Next, stopcock No. 16 was closed, the cooling bath was removed from J, and all but the lower $1\frac{1}{2}$ inches of the reaction chamber (J) was enclosed in an aluminum foil jacket such that powdered Dry Ice could be placed in the jacket to cool the upper part of J. This was done in order to be able to reflux the solution of potassium metal thus speeding up the conversion of the potassium to potassium amide. The time required for the reaction depended upon the activity of the catalyst. It varied from several hours to several days. The pressure in this part of the system was monitored at all times with the manometer. When conversion was complete, care being taken to wash down with liquid ammonia any potassium that might have splashed on the walls of the chamber or on the fritted disc, the foil jacket was removed, and chamber (J) was again immersed in the cooling bath. The hydrogen that had been formed was removed by opening stopcock No. 11 several times for a few seconds at a time. Next, the potassium amide solution was transferred to the storage flask (D). To do this D was immersed in a Dry Ice-acetone

bath, and the cooling bath was removed from J. J was then inverted so that the solution was filtered into D. Stopcock No. 16 should still be closed during this operation. To insure completeness of transfer of the potassium amide some of the ammonia was distilled back into J. This was accomplished by replacing a bath around J and removing the cooling bath from D. This allowed ammonia to distill from D to J. After 25-30 ml. had been distilled, the liquid ammonia was filtered back into D in the manner previously described. The rinsing operation was done at least three times. Since the storage flask (D) was a volumetric flask, a standard solution of potassium amide was prepared by diluting the amide solution already in the flask to the fiducial mark. This was accomplished by distilling ammonia from the drying chamber (B) to D in the manner already described. During the dilution, the cooling bath around D was maintained at $-60^{\circ} \pm 1^{\circ}$, as this is the temperature of the liquid ammonia solution in the spectrophotometric cells during their use.¹¹ The cooling bath was acetone kept at the desired temperature by the addition of Dry Ice. After the dilution was complete, stopcocks No. 8 and 9 were closed. They were kept closed, except when the potassium amide solution was being transferred to the spectrophotometric cells. At this point in the procedure stopcocks No. 1, 2, 3, 4, 8, 9, 10, 11, 12 and 16 were closed. Of these, Nos. 1, 2, 3, 10, 12 and 16 were kept closed throughout the rest of the procedure.

The spectrophotometric cells were filled in the following manner. Stopcock No. 6 was closed, the cap at point C was removed, and a cell was attached at this point. Stopcock No. 6 was then opened and the line was evacuated. The only stopcocks open during the evacuation of the line were Nos. 5, 6, 7, 11, 13, 14, 15 and 17. Oxygen was again removed from this part of the system by the evaporation-evacuation procedure described earlier. Next stopcocks No. 6, 11 and 17 were closed, and No. 9 was opened so that the amide solution could be thawed. During the thawing of the amide solution, the pressure in this part of the system was watched closely and kept below atmospheric pressure. During this time that part of the line between C and D was enclosed in an aluminum foil trough, the vacuum-jacketed end of the spectrophotometric cell was immersed in a Dry Ice-acetone bath, and the cooling jacket of the cell was filled with a Dry Ice-acetone mixture. The foil trough was then filled and kept filled with powdered Dry Ice. When the amide solution had thawed, the delivery tube leading to stopcock No. 8 was filled with the amide solution. The delivery tube was filled by allowing the amide solution to warm to the point where the ammonia pressure above the solution forced it into the tube. Two things needed to be watched carefully during this step, (1) the pressure had to be watched at all times and maintained below atmospheric pressure, and (2) the foil trough had to be kept full of Dry Ice. When the delivery tube had been filled, stopcock No. 8 was opened, and the line

leading to the cell was filled. Stopcock No. 17 was then opened long enough to allow approximately 3 ml. of amide solution to enter and then closed. While the cell was being filled, the bath enclosing the end of the cell was removed to aid in judging the length of time stopcock No. 17 was to be held open, but the cell jacket was kept filled with coolant. When the transfer was complete, D was immersed in the cooling bath, and the aluminum foil trough was removed. When the line had warmed to room temperature, stopcock No. 8 was closed, and when the pressure had returned to normal (the pressure of liquid ammonia at -78°), stopcock No. 9 was closed. The cell was removed from the system, and C was either capped, or another cell was attached. As the cell was being removed, a stream of dry nitrogen was directed past the opening. The cell was stoppered as soon as it was disengaged from the line. During the transfer of the amide solution, the only stopcocks to be opened and closed were Nos. 6, 8, 9 and 17. All others were as previously noted.

In order to get a qualitative comparison of the acidity of several compounds, a few simple experiments were run. The potassium amide was prepared by dissolving a weighed amount of potassium metal in liquid ammonia to which had been added a very small crystal of ferric nitrate (catalyst). The solution was refluxed until the reaction was complete. Next an excess of one acid was added, and after a few minutes another acid was added. The second acid was added in small portions

(10-20 mg.). The total amount added depended upon whether or not a reaction (as evidenced by a color change) was noted with the first addition. In some cases an excess of the second acid was added. The presence or absence of colors was used to compare acidities. The following compounds were used: tris(ethylthio)methane, bis(methylthio)methane, bis(phenylthio)methane, *p*-toluidine, fluorene, xanthene, 9-phenylxanthene and *m*-trifluoromethylaniline.

Dimethyl Sulfoxide-Potassium *t*-Butoxide.--After the work in liquid ammonia was well under way, Gram and coworkers¹³ pointed out that some solvents appeared to enhance the basicity of alkoxide ions. In particular they found that potassium *t*-butoxide was a stronger base in dimethyl sulfoxide than in *t*-butyl alcohol. Accordingly, we decided to run a few experiments to see whether or not such a system might be useful for studying the acidity of very weak acids. In a typical experiment a small amount (10-100 mg.) of an acid was added to a solution of potassium *t*-butoxide in dimethyl sulfoxide under dry nitrogen, and the presence or absence of the color characteristic of the conjugate base of the acid was noted. The following compounds were used in these experiments: triphenylmethane, diphenylmethane, α -benzylnaphthalene, *p,p'*-bis(dimethylamino)diphenylmethane, and toluene. The results are shown in Table 4, p. 30.

¹³D. J. Gram, B. Rickborn, and G. R. Knox, J. Am. Chem. Soc., **82**, 6412 (1960).

Spectrophotometric Method

A special spectrophotometer cell (see Fig. 1) had been developed for use in the Beckmann DK-1 Recording Spectrophotometer, with which the visual absorption spectra of liquid ammonia solutions could be measured.

Because it was very time-consuming to change the contents of a cell, the DK-1 was operated by use of a secondary standard. This was done in the following manner. Two cells were filled with the amide solution and placed in the cell compartment of the DK-1. The cells were covered with a heavy black cloth. The cloth also covered the cell compartment. The 0-100 per cent transmission lines were adjusted for a wavelength corresponding to the absorption maximum of the anion to be studied. Next the cells were replaced with two pieces of square pyrex tubing, one of which was darkened slightly on the inner faces with black ink. The per cent transmission observed without changing the machine settings was recorded. Then when a measurement was to be made, the pieces of square tubing were placed in the DK-1, and the machine was so adjusted that this per cent transmission reading was reproduced. The pieces of tubing were then removed, and the measurement was made using the cells.

The extinction coefficient of a compound is determined in the following manner. A definite amount of an acid in ether solution was placed in a cell by means of a syringe. The ether was removed in vacuo with an aspirator. The cell

was then placed in the system and filled in the manner described previously. An excess of amide was added in all experiments; however, the size of the excess depended upon the concentration of the amide solution. Before a measurement was made, the solution was allowed to stand for at least one hour. The vacuum-jacketed portion was not cooled, but the cooling jacket was kept filled with a Dry Ice-chloroform mixture. With this mixture in the cooling jacket the temperature of the liquid ammonia solution within the cell is -60° .¹¹ The absorption of the anion at several concentrations was measured to learn whether or not Beer's law was obeyed; in all cases it was.

The procedure for measuring an equilibrium constant was the same, except that two acids were present in the cell. One of the acids had a colorless anion, so that only one species, for which the extinction coefficient was already known, needed to be measured spectrophotometrically.

Reagents

Ethylenediamine.--Eastman White Label ethylenediamine was distilled from sodium, b.p. $114-115^{\circ}$; reported value 117° .¹⁴

t-Butylamine.--Eastman White Label t-butylamine was distilled from Na-K alloy (1-5), b.p. 45° ; reported $44-44.5^{\circ}$.¹⁵

¹⁴J. T. Clarke and E. R. Blout, J. Polymer Sci., **1**, 419 (1946).

¹⁵L. E. Smith and O. H. Emerson, Org. Syntheses, **29**, 18 (1949).

Diethyl Ether.--Mallinkrodt absolute ether was dried over sodium wire.

Dimethyl Sulfoxide.--Baker's analyzed reagent dimethyl sulfoxide was used without further purification.

Potassium t-Butoxide.--Potassium metal was dissolved in Eastman White Label t-butyl alcohol. The excess alcohol was removed in vacuo. The white salt was dried in vacuo at 80°.

Potassium.--Baker's potassium metal was used without purification.

Potassium Ampoules.--A special piece of equipment was used to prepare the potassium ampoules (see Fig. 2). It consisted of a thin-walled bulb 5 mm. in diameter connected to a 10/30 standard taper joint by a neck 20-30 mm. long and 2 mm. O. D. A small piece of potassium was placed in a tube that had been cleaned and weighed, and the tube with contents was inserted into the high-vacuum system at point F. A slight excess of nitrogen pressure, ca. 5 mm. was placed between stopcocks No. 4, 6 and 7. Stopcocks No. 10 and 11 were opened and the sys-

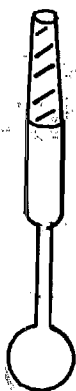


Figure 2. Potassium Ampoule Bulb

tem was evacuated. Stopcock No. 9 was kept closed the whole time. After the system had been pumped on for 3-4 hours, stopcock No. 11 was closed. The potassium metal, resting at the constriction, was heated gently with a luminous flame. The metal would melt, but not break through the oxide film! If done properly, the metal ball would close the constriction. Stopcock No. 7 was then opened and the molten metal was forced into the ball of the tube by the nitrogen pressure. The oxide film was left on the walls of the tube. After allowing the metal to cool, and evacuating the line again, the bulb was sealed off at some point in the narrow neck. The part remaining in the system was removed, cleaned and dried. The two pieces were weighed, and the difference in weight from that of the empty tube was the weight of potassium in the bulb. The ampoules were prepared when the system was not being used to handle liquid ammonia.

Ammonia.--Matheson Co. ammonia was dried with sodium metal.

9-Phenylxanthene.--9-Phenylxanthene was prepared by the method of Gomberg and Nishida,¹⁶ m.p. 143-144°; reported m.p. 144-145°.¹⁶

p-Toluidine.--Eastman White Label p-toluidine was fractionally distilled before using. The fraction boiling at 114-115°/30 mm. was collected and used.

Triphenylmethane.--Eastman White Label triphenylmethane was used without purification.

¹⁶M. Gomberg and D. Nishida, J. Am. Chem. Soc., 45, 190 (1923).

Tris(ethylthio)methane.--See part II p. 44 of this thesis.

Bis(methylthio)methane.--See part II p. 39 of this thesis.

Bis(phenylthio)methane.--See part II p. 44 of this thesis.

Xanthene.--H. M. Chemical Co. xanthene was used without further purification.

Fluorene.--Eastman technical grade fluorene was recrystallized from ethanol, m.p. 113-114°; reported m.p. 114-114.5°. ¹⁷

m-Trifluoromethylaniline.--m-Trifluoromethylnitrobenzene, prepared by the method of Swarts, ¹⁸ was reduced with tin and hydrochloric acid. 12.11 g. (0.063 mole) of the nitro compound was mixed with 13.2 g. (0.11 mole) of granulated tin, and 27 ml. of conc. hydrochloric acid was added slowly with cooling. After the addition of the hydrochloric acid was complete, the mixture was then cooled, and a solution containing 75 g. of sodium hydroxide in 100 ml. of water was added until the mixture was strongly alkaline. The mixture was steam distilled, and the distillate was saturated with sodium chloride and then extracted three times with 100 ml. portions of ether. The ether extracts were dried overnight with solid sodium hydroxide. Next, the ether was removed in vacuo on a steam bath, and the liquid residue was taken up in 30 ml. of glacial acetic acid. Ten milliliters of acetic anhydride was added to this solution, and the resulting solution was heated for 2 hrs. on

¹⁷ N. S. Capper and J. K. Marsh, J. Chem. Soc., 724 (1926).

¹⁸ F. Swarts, Bull. sci. Acad. roy. Belg., 1920, 389; C. A., 16, 2316 (1922).

a steam bath. After cooling slightly, the reaction mixture was poured into cold water, and the pale yellow crystals which precipitated were removed by filtration. These crystals were recrystallized three times from benzene-hexane to yield a white crystalline product, m.p. 103-104°. m-Trifluoromethylacetanilide has a melting point of 103.5°. ¹⁸ The acetanilide was hydrolyzed with potassium hydroxide in ethanol. Twenty grams of the m-trifluoromethylacetanilide in 40 ml. of refluxing ethanol was mixed with a solution containing 12 g. of KOH in 6 ml. of water. The resulting mixture was heated for an additional hour on a steam bath, then 75 ml. of water was added, and the colorless oil that separated was removed. The oil was dried overnight over solid potassium hydroxide and vacuum distilled to yield approximately 2 ml. of a clear liquid, b.p. 89-90°/20 mm. The reported boiling point is 86°/20 mm. ¹⁹ Vapor phase chromatography showed only one compound was present.

Platinum Black Catalyst.—Platinum gauze was used in preparing the platinum black catalyst. The gauze was platinized using the method of Jones and Bollinger. ²⁰ After platinization the catalyst was stored in distilled water until use. The shortest reaction times were obtained with catalyst that had not been previously used. The reason for this is unknown, for it should be possible to clean the catalyst surface and reuse it. How-

¹⁹R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 71, 3838 (1949).

²⁰G. Jones and D. Bollinger, J. Am. Chem. Soc., 57, 280 (1935).

ever, it was never found possible to do this, even though ethanol, acetone and chromic acid solution were used in the attempts to clean the catalyst surface.

Square Pyrex Tubing.--The 8 mm. I. D. and 12 mm. I. D. square pyrex tubing used in the special spectrophotometric cell (see Fig. 1) was obtained from the Fisher-Porter Co.

Synthesis of 1-Phenyl-1-(2-hydroxyphenyl)ethanol.--A phenyl Grignard reagent that had been prepared from 31.4 g. (0.20 mole) of bromobenzene and 4.8 g. (0.20 mole) of magnesium turnings in 100 ml. of dry ether was allowed to react with 13.6 g. (0.10 mole) of *o*-hydroxyacetophenone. The reaction mixture was allowed to reflux for one hour, poured into iced sulfuric acid, and the ether layer separated and saved. The ether layer was dried over anhydrous magnesium sulfate, and the ether was removed in vacuo. The crude product was recrystallized several times from ethanol-water to yield white crystals, m.p. 113-114°. A sample was sent to Clark Microanalytical Laboratories, Urbana, Illinois, for analysis.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 79.29, 79.12; H, 6.40, 6.62.

The infra-red spectrum of a Nujol mull of this compound is consistent with the compound being 1-phenyl-1-(2-hydroxyphenyl)-ethanol. The following maxima are listed in decreasing order of intensity: 13.25 μ , 14.12 μ , 8.04 μ , 8.15 μ , 12.96 μ , 9.56 μ , 11.07 μ , 3.60 μ , 2.84 μ , 7.70 μ , 8.92 μ , 9.32 μ , 9.05 μ , 10.89 μ , 11.50 μ .

CHAPTER III

RESULTS

The following data were obtained in determining the equilibrium constant for the reaction of 9-phenylxanthene with potassium toluidide in liquid ammonia at -60° . A 0.814 cm. cell was used in all experiments.

Table 2. Extinction Coefficient of
the 9-Phenylxanthide Ion

Absorbance (at 493 m μ)	Concentration $\times 10^5$ m./l.	$10^{-4} \epsilon$ (l./mole-cm.)
0.18	1.00	2.21
0.30	1.82	2.03
0.41	2.21	<u>2.28</u>
	ave.	2.17 ± 0.10

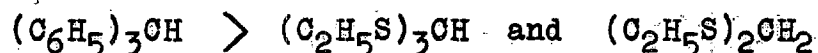
Table 3. Equilibrium Measurements for 9-Phenylxanthene
and Potassium p-Toluidide

Run	1	2
Potassium Amide added	74.9 x 10 ⁻⁴ mmole.	14.2 x 10 ⁻⁴ mmole.
p-Toluidine added	125 x 10 ⁻⁴ mmole.	31.0 x 10 ⁻⁴ mmole.
9-Phenylxanthene added	1.73 x 10 ⁻⁴ mmole.	0.87 x 10 ⁻⁴ mmole.
Volume of solution	3.84 ml.	3.38 ml.
Absorbance at 493 mμ	0.678	0.362
K ^a	4.0	5.0
ΔpK _a (-log K)	0.60	0.70

^aK is the equilibrium constant for the following reaction: $\text{XH} + \text{T}^- \rightleftharpoons \text{X}^- + \text{TH}$, thus $K = \frac{(\text{X}^-)(\text{TH})}{(\text{XH})(\text{T}^-)}$, where XH and X⁻ are 9-phenylxanthene and 9-phenylxanthide ion, respectively, and TH and T⁻ are p-toluidine and p-toluidide ion respectively.

The experiments whose results will be given in the following paragraphs were run in order to find two compounds of comparable acidity. The results of one of these experiments led to the use of the pair 9-phenylxanthene-p-toluidine in the quantitative experiments described in Tables 2 and 3. The reactions were carried out with potassium amide in liquid ammonia.

In one such experiment 10-20 mg. of triphenylmethane was added to a solution containing equimolar amounts of bis(methylthio)methane and its conjugate base. The bright red-color of the triphenylmethide ion was produced instantly, even though there was present a ten-fold excess of the conjugate base of the sulfur compound over the triphenylmethane. The addition of this amount of triphenylmethane to a solution of potassium amide produced the same intensity of color. When tris(ethylthio)methane was added to the original solution, no diminution in color could be detected. This was true even though a ten-fold excess of the tris- compound to triphenylmethane (over the amount of amide originally present) was added. These results suggested the following order of acidity:



The two sulfur compounds could not be compared directly, because their conjugate bases are the same color.

In another such experiment diphenylmethane was compared with tris(ethylthio)methane. After an excess of the sulfur

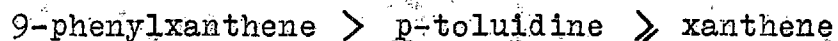
compound had been added to a solution containing potassium amide, a small amount of diphenylmethane was added. The yellow-green color of the tris(ethylthio)methide ion remained. After one hour the color of the solution had become an orange-brown. It is not clear whether the color change was due to the diphenylmethide ion which is reddish-brown in color or to the decomposition of the tris(ethylthio)methide ion described in part II of this thesis.

In trying to find a compound of acidity comparable to that of fluorene, fluorene was compared with p-toluidine and m-trifluoromethylaniline. In the experiment with p-toluidine, 0.4 mmole. of p-toluidine was added to a solution containing 0.9 mmole. of potassium amide, and then fluorene (approx. 0.06 mmole. was added. An intense orange-brown color developed. The intensity of the color of the fluorenyl ion was the same as that obtained when only potassium amide was present. When the same type of experiment was carried out with fluorene and m-trifluoromethylaniline, the same results were obtained. The following order of acidity is written for these compounds:

fluorene > p-toluidine and m-trifluoromethylaniline

The last experiment of this type was carried out using p-toluidine, xanthene and 9-phenylxanthene. First 6 mmole. of p-toluidine was added to a solution containing 2 mmole. of potassium amide, and then a small amount of xanthene (0.1-0.2 mmole.) was added to the yellow-green solution and a faint

pink color developed. Upon the addition of 0.04-0.08 mmole. of 9-phenylxanthene, a much brighter red color developed instantly. This suggests the following order of acidity:



The extinction coefficients of the conjugate bases of the hydrocarbon acids seem from experience and from some experiments¹¹ to be very large. Thus the presence of a small amount of one of these anions gives intense color to a solution.

A few experiments were made using potassium t-butoxide in dimethyl sulfoxide. The acid was added to a solution of potassium t-butoxide in dimethyl sulfoxide under dry nitrogen, and the presence or absence of color was noted.

Table 4. Colors Obtained with t -BuOK-Me₂SO and
Various Weak Acids

Acid	Color
Triphenylmethane	Red
α -Benzyl-naphthalene	Blue
Diphenylmethane	Red-Orange
Tris(ethylthio)methane	Green-Yellow
p,p' -Bis(dimethylamino)di- phenylmethane	Red-Brown (formed slowly)
Toluene	NO COLOR

The results shown in Table 4 are very similar to those obtained in similar experiments with potassium amide in liquid ammonia.¹¹

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The original intent of this work was to find a suitable method for studying quantitatively the strength of very weak acids. This goal seems to have been reached with the procedure described for the comparison of the acidity of 9-phenylxanthene and *p*-toluidine. Although time-consuming and still in need of some refinements, the method is reliable, and the data are reproducible.

The work of Conant and Wheland² and McEwen³ shows 9-phenylxanthene to be an acid at least 2 pK_a units weaker than *p*-toluidine. In our solvent-base system, however, 9-phenylxanthene is a stronger acid than *p*-toluidine by 0.65 pK_a units. The large disparity between our value and theirs can be attributed to (1) solvent effects, (2) our more sensitive analytical methods and (3) the possibility that these two compounds were not actually compared in the other studies. Our qualitative experiments showed 9-phenylxanthene to be a stronger acid than xanthene. McEwen³ listed these compounds as having the same pK_a .

The studies in dimethyl sulfoxide show the *t*-butoxide ion to be at least as strong a base in this solvent as the amide ion is in liquid ammonia. The results shown in Table 4

indicate that in dimethyl sulfoxide t-butyl alcohol is as weak an acid as diphenylmethane or weaker. McEwen³ found t-butyl alcohol to be at least 19 pK_a units stronger than diphenylmethane in the solvents he used. The large difference seems to be a solvent effect.

CHAPTER V

RECOMMENDATIONS

Before going any further with the work in liquid ammonia, additional experiments should be made with potassium t-butoxide in dimethyl sulfoxide. If an experimental method can be found for this solvent-base pair, the work in liquid ammonia will be unnecessary, except to compare acidities in the two systems.

There are additional things that could be done in the potassium amide-liquid ammonia work. The most obvious of these is the extension of the range of acidities studied. This should be done at both ends of the acidity scale. In order to make this study somewhat easier, there are some improvements that should be made. Some way should be found to standardize the manufacture of the spectrophotometric cells. The optical properties of the individual cells vary widely. Much of the variance comes in the fabrication of the cells, and this could be eliminated by a better method for aligning the double walls of the cells. In addition a better cell holder should be made. A cell holder is needed that does not allow any variance in the cell position. Last but not least a durable spectrophotometer is needed.

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PART TWO

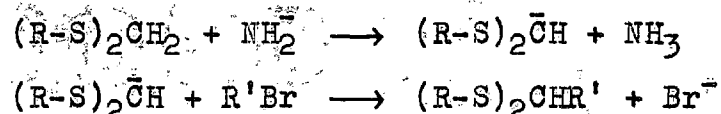
THE REACTION OF ETHYL ORTHOTHIOFORMATE AND
RELATED COMPOUNDS WITH POTASSIUM AMIDE IN

LIQUID AMMONIA

CHAPTER I

INTRODUCTION

As a part of the study of the acidity of very weak acids, some acids were needed whose anions are colorless. Arens and coworkers¹ had reported that bis(alkylthio)methanes were alkylated by alkyl halides after prior reaction with potassium amide in liquid ammonia. They suggested the following reaction scheme:

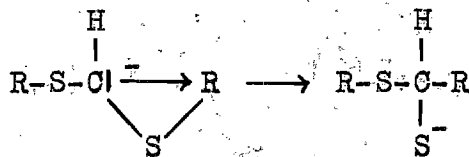


Since the negative charge is not spread by resonance over any large volume, we hoped that the anions of bis(alkylthio)methanes would be colorless, and for this reason a compound of this type, as well as a bis(arylthio)- and a tris(alkylthio)methane was investigated.

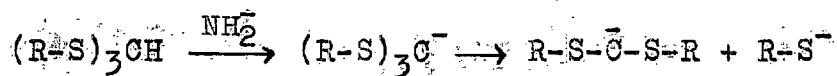
Before such compounds could be used in the acidity study, their reactions with potassium amide in liquid ammonia had to be studied. This was necessary to eliminate the possibility of complicating side reactions. It seemed to us that

¹J. F. Arens, M. Fröling and A. Fröling, Rec. trav. chim., 78, 663 (1959).

the anions of both the di- and trisubstituted compounds could undergo a Stevens-type rearrangement²



There was also the possibility that these compounds would undergo an α -elimination reaction in the presence of such a strong base as the amide ion



The work to be described here was undertaken to investigate these possibilities and thus to see if the bis- and tris(alkylthio)methanes and bis(arylthio)methanes could be of use in the study of weak acids.

²J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 116.

CHAPTER II

PROCEDURE

Preparation of Bis(methylthio)methane.--41.5 g. of a 37 per cent formalin solution (0.5 mole of aldehyde) and 48 g. (1.0 mole) methyl mercaptan were mixed together in a 3-necked 200 ml. round-bottom flask equipped with a Dry Ice-acetone condenser. Sufficient dioxane (approx. 10 ml.) was added to make the mixture homogeneous, and then 2.5 ml. of conc. hydrochloric acid was added. The mixture was allowed to stand for 25 hours. The Dry Ice-acetone condenser was used only during the initial mixing period. During this time two layers appeared. The two layers were separated, and the organic layer was dried overnight over anhydrous magnesium sulfate and distilled. The fraction boiling at $145-157^{\circ}$ was collected for redistillation. There was considerable foaming during the distillation. The $145-157^{\circ}$ fraction was fractionally distilled through a 6 inch Vigreux column to yield 19.5 g., b.p. $148-151^{\circ}$; reported b.p. $148^{\circ}/755$ mm.³

The oxidation of 0.15 g. of the bis(methylthio)methane to the corresponding disulfone with 30 per cent hydrogen peroxide in glacial acetic acid yielded an unweighed amount of white crystals, m.p. $145-149^{\circ}$. After two recrystallizations

³H. Böhme, R. Frank and W. Krause, Ber., 82, 433 (1949).

from ethanol-water the bis(methylsulfonyl)methane had a melting point, 145-147°; reported m.p. 145°. ³

Reaction of Bis(methylthio)methane with Potassium Amide in

Liquid Ammonia.--The overall reaction described herein is of the type described by Arens et al., ¹ who gave no experimental details and did not state what specific compounds were studied.

A 300 ml. three-necked flask was equipped with a Dry Ice-acetone condenser, a stopper, and a 90° connecting tube. The connecting tube was attached to a Y-tube through which a stream of dry nitrogen was passing. The flask was immersed in a Dry Ice-acetone bath and 100 ml. of liquid ammonia was condensed in the flask. A crystal of ferric nitrate, catalyst for the conversion of potassium to potassium amide, was added along with 3.9 g. (0.1 mole) of potassium metal. The solution was refluxed until the conversion of the potassium to potassium amide was complete usually 20-30 minutes. Next 5.0 g. (0.046 mole) of bis(methylthio)methane was introduced. The colorless solution became greenish-yellow in color. It was allowed to reflux for 6-7 hours, then cooled to -60° and 9.09 g. (0.1 mole) of n-propyl bromide added. After an additional 45 min. reflux time, 50 ml. of absolute ethanol was added, and the mixture was allowed to warm to room temperature. Fifty milliliters of water was added, and the mixture was extracted three times with 25 ml. portions of ether. The ether extracts were dried with anhydrous magnesium sulfate, and the ether was removed in vacuo. The residue was fractionally dis-

tilled to yield 2.31 g. of a colorless liquid, b.p. 96-98°/30 mm., n_D^{10} 1.5128. A portion of the liquid was oxidized with peroxypropionic acid to give a white crystalline solid, m.p. 93-96°. This compound was later shown to be 1,1-bis(methylthio)butane (see the next section).

Vapor-phase chromatography of the liquid described above revealed no significant amounts of other products.

Preparation of 1,1-Bis(methylsulfonyl)butane.--The preparation of 1,1-bis(methylthio)butane from n-butyraldehyde and methyl mercaptan was carried out by a method analogous to that used by Wolfrom and Karabinos⁴ for related compounds. From 7.2 g. (0.1 mole) of n-butyraldehyde and 13 g. (0.27 mole) of methyl mercaptan was obtained 5.0 g. of product: b.p. 93-94°/28 mm.; $n_D^{13.5}$ 1.5114; $d_4^{13.5}$ 0.991; molar refractivity calcd. for n-C₃H₇CH(SCH₃)₂: 45.46, found: 45.85 (atomic and structural constants from ref. 5). The assigned structure is supported by the method of synthesis and by oxidation to the corresponding disulfone. A 0.15 g. sample of this compound was oxidized with peroxypropionic acid to give 0.1 g. of white crystalline solid, m.p. 93-96°. An analytical sample was sent to Galbraith Microanalytical Laboratories, Knoxville, Tennessee for elemental analysis.

⁴M. L. Wolfrom and J. V. Karabinos, J. Am. Chem. Soc., **66**, 909 (1944).

⁵N. A. Lange, Handbook of Chemistry, 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 1421.

Anal. Calcd. for $C_6H_{14}O_4S_2$: C, 33.63; H, 6.58; S, 29.92.

Found: C, 33.58; H, 6.31; S, 30.14.

Mixed melting points using equal amounts of this sulfone and the one prepared in the previous section showed no depression.

Reaction of Tris(ethylthio)methane with Potassium Amide in

Liquid Ammonia.--The procedure used in this reaction was the same as that previously described for bis(methylthio)methane. Sixty ml. of liquid ammonia, 0.60 g. (0.015 mole) of potassium metal, a crystal of ferric nitrate, and 1.05 g. (0.005 mole) of tris(ethylthio)methane were used. After the addition of the sulfur compound, the solution was allowed to reflux 10-12 hours. During the reflux period the color of the solution changed from a yellow-green to an orange-brown. The ammonia was then removed by distillation. Dilute acetic acid was added to the residue, and any gases given off were condensed in a trap immersed in a Dry Ice-acetone bath. Although ethyl mercaptan could not be shown to be present by infra-red measurements, its characteristic odor was easily detectable in the trap.

The solid residue from the reaction (0.06 g.) was recrystallized from pentane to give white needles, m.p. 50-53°.

An authentic sample of tetrakis(ethylthio)ethylene prepared from tetrachloroethylene and sodium ethylmercaptide by the method of Claesson⁶ had a melting point of 50-53°. The

⁶P. Claesson, J. prakt. Chem., [2] 15, 193 (1877).

melting point of a mixture of equal amounts of the two compounds showed no depression. The infra-red spectra of the two compounds were identical.

Reaction of Bis(phenylthio)methane with Potassium Amide in Liquid Ammonia.---

The procedure used was the same as that used in the experiments with bis(methylthio)methane. In all cases there was a several-fold excess of amide to sulfur compound, sometimes as high as 9 to 1. After the addition of the sulfur compound, the solution was allowed to reflux for 3-4 hours. At the end of this time either the ammonia was allowed to evaporate, or ethyl alcohol was added to stop the reaction.

In those experiments in which the ammonia was removed by distillation, the residue was treated with water, extracted with ether, and then acidified with glacial acetic acid. This acid solution was then titrated with 0.1 N iodine solution.

In the experiments in which ethyl alcohol was used to stop the reaction, after the addition of the alcohol the ammonia was removed by distillation. Water was added to the residue, and the solution was extracted with ether. The water layer was acidified with glacial acetic acid and titrated with 0.1 N iodine solution.

The iodine titration was done to see if any mercaptan was present, i.e. to see if mercaptide ion had been formed in the reaction.

Reagents.---The ammonia was obtained from the Matheson Co. and was used without purification. The potassium metal, from the

J. T. Baker Co., was also used without purification. Ferric nitrate nonahydrate was also obtained from the J. T. Baker Co. The method of Houben and Schultze⁷ was used for the preparation of tris(ethylthio)methane, b.p. 76°/0.1 mm., reported b.p. 116°/10 mm. Peroxypropionic acid was prepared by the method of Barker and MacDonald.⁸ The fraction having a b.p. 25-30°/16 mm. was collected and used. The method of Fromm⁹ was used for the preparation of bis(phenylthio)methane, m.p. 34-36°, reported m.p. 34-35°.¹⁰

⁷ J. Houben and K. M. L. Schultze, Ber., 44, 3235, (1911).

⁸ R. Barker and D. L. MacDonald, J. Am. Chem. Soc., 82, 2297 (1960).

⁹ E. Fromm, Ann., 253, 135 (1889).

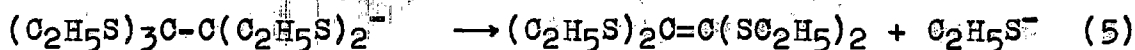
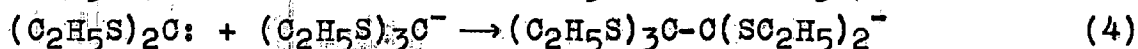
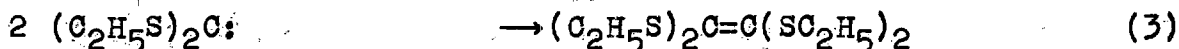
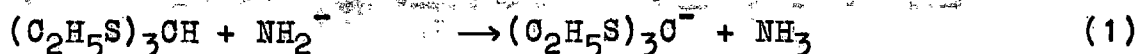
¹⁰ F. G. Bordwell and B. M. Pitt, J. Am. Chem. Soc., 77, 572 (1955).

CHAPTER III

RESULTS AND DISCUSSION

Bis(methylthio)methane reacted in the manner reported by Arens et al.¹ No evidence for any rearranged product could be found. This compound should be useful in the study of very weak acids.

Tris(ethylthio)methane, on the other hand, did not give a very stable anion upon reaction with potassium amide in liquid ammonia. The reaction products indicate an α -elimination reaction. The following reaction mechanism is suggested:



The formation of the methylene intermediate, steps (1) and (2), is written as a step-wise process for the following reasons:

(a) Slauch and Bergman¹¹ found that tris(ethylthio)methane undergoes base-catalyzed hydrogen exchange, and (b) a greenish-yellow color develops in the reaction mixture as soon as

¹¹ L. H. Slauch and E. Bergman, J. Org. Chem., **26**, 3158 (1961).

the sulfur compound is added to the amide solution. The color is the same as that of the bis(methylthio)methide ion and seems to be characteristic of these carbanions. The color did not seem to fade throughout the time of reaction, although it did change to an orange-brown. Thus it seems that step (2) is a slow one. This would also account for the low yield of tetrakis(ethylthio)ethylene. The methylene intermediate formed in step (2) is the first one known to have two sulfur atoms attached directly to the divalent carbon atom. Step (3) is probably unimportant in solutions as dilute as these, but in the absence of evidence to the contrary it cannot be overlooked.

The results obtained from the experiments with bis(phenylthio)methane are somewhat confusing. Additional experiments are necessary. In those experiments in which ethyl alcohol was added to stop the reaction little or no mercaptide ion was formed (usually less than 10 per cent), and unreacted starting material was recovered in good yield. In those experiments in which the ammonia was allowed to distill from the reaction mixture without quenching the reaction, considerable mercaptide was produced, perhaps because of the higher temperatures to which the carbanion was exposed in these cases. The yield ranged from 0.33 to more than 1.00 mole per mole of reactant.

CHAPTER IV

CONCLUSIONS

The evidence for the formation of bis(ethylthio)methylene as an intermediate in the reaction of tris(ethylthio)methane with potassium amide, while not conclusive, is very strong. It is difficult to write other reasonable mechanisms that give the observed products.

The bis(ethylthio)methylene should be stabilized by both p and d orbital resonance with the adjacent sulfur atoms. The vacant p-orbitals of the central carbon atom can overlap with the filled p-orbitals of the sulfur atoms, while the unshared pair of electrons present at the methylenic carbon are stabilized by overlap with the vacant d-orbitals of the sulfur atoms. This type of resonance with sulfur is not new.¹² Methylthiofluoromethylene, an intermediate in the reaction of difluorochloromethane with sodium thiomethoxide,¹³ probably gains some of its stability from p and d orbital resonance with sulfur. In addition the ease of formation of bis(methylthio)methide ions seems likely to be due partly to the stabilization of the negative charge by the methylthio groups.

¹²W. von E. Doering, and A. K. Hoffmann, J. Am. Chem. Soc., 77, 521 (1955).

¹³J. Hine and J. J. Porter, ibid., 82, 6118 (1960).

The low yield of tetrakis(ethylthio)ethylene is probably due to incomplete decomposition of the tris(ethylthio)methide ion, as well as to the fact that there was a five-fold excess of amide ions over the tris(ethylthio)methide ions and an even larger excess of ammonia. Thus the combination of the intermediate methylene with ammonia or an amide ion rather than a tris(ethylthio)methide ion is strongly favored by concentration effects.

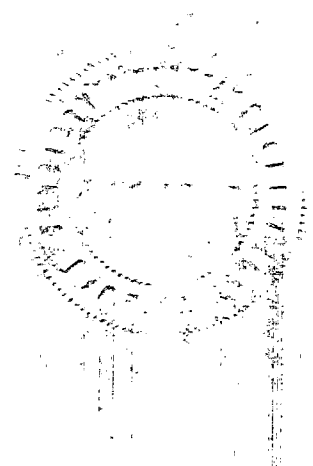
As was mentioned before, the results obtained from the experiments with bis(phenylthio)methane are somewhat uncertain. It seems likely that this compound does undergo some elimination, however, the extent of this reaction needs further study. In those cases in which mercaptide ion was produced we were unable to identify any other products.

CHAPTER V

RECOMMENDATIONS

The reaction of tris(ethylthio)methane with potassium amide was by no means studied exhaustively. A complete product study should be made in order to see what other reaction paths the bis(methylthio)methylene takes. It seems likely that this methylene intermediate can also be generated by potassium t-butoxide in dimethyl sulfoxide. This possibility should be investigated further. This solvent-base system would be much more convenient than liquid ammonia-potassium amide.

The effect of substituents upon the reaction should be studied. This could be done in two ways: (1) substituents could be placed directly in the alkyl group; (2) various substituted aryl groups could be used in place of the alkyl groups.



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VITA

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